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| (54) Title: SALINE SOLUBLE INORGANIC FIBRES  |  |  |  |
| (57) Abstract  |  |  |  |
| The use of P <sub>2</sub> O <sub>5</sub> and/or B <sub>2</sub> O <sub>3</sub> as a component to improve the refractoriness of inorganic fibres comprising SiO <sub>2</sub> , and CaO and/or MgO is described. The inorganic fibres have a composition such that SiO <sub>2</sub> + P <sub>2</sub> O <sub>5</sub> -(58 + (if MgO > 10, 0.5 x (MgO-10) else 0)) > -2.4 wt.%.   |  |  |  |

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SALINE SOLUBLE INORGANIC FIBRES

This invention relates to saline soluble inorganic fibres.

Saline soluble inorganic fibres have been described in several patent specifications, see for example WO93/15028. Fibres are required to be soluble in saline solution so that inhaled or ingested fibres dissolve rather than providing a source of irritation or otherwise affecting health. WO93/15028 showed that fibres comprising  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{MgO}$  and having a silica content of greater than 58% (or greater than 58% plus 0.5 times (wt%MgO - 10) if  $\text{MgO} > 10\text{wt}\%$ ) had suitable shrinkage characteristics at  $800^\circ\text{C}$  and  $1000^\circ\text{C}$  to be usable as refractory materials. A further feature of WO93/15028 was the use of the percentage of non-bridging oxygens present to predict the solubility of fibres in physiological saline solution.

Various subsequent applications have described the effect of  $\text{P}_2\text{O}_5$  and  $\text{B}_2\text{O}_3$  on solubility - see for example WO95/29135.  $\text{P}_2\text{O}_5$  is alleged to have a solubilising effect on such fibres.

The German government have proposed a fibre classification which turns on a variable  $K_I$  which is defined as:

$$K_I = \Sigma(\text{Na, K, B, Ca, Mg, Ba -oxide}) - 2 * \text{Al-oxide}$$

(the amounts of the oxides being expressed as weight %)

According to the proposed fibre classification if  $K_I$  is greater than 40 the fibre requires no health warnings. If  $K_I$  lies between 30 and 40 the fibre requires health warnings to be made. If  $K_I$  is less than 30 more serious marking is required (it is labelled as a carcinogen). It is readily apparent that it is difficult to provide a high  $K_I$  fibre ( $K_I > 40$ ) while still providing a refractory fibre like that of WO93/15028 ( $\text{SiO}_2 > 58\text{wt}\%$ ), there being a very narrow window of compositions to meet.

As a result of investigating fibre compositions that may meet the fibre classification and yet still be refractory enough to meet the standard of WO93/15028 (shrinkage of less than 3.5% at both  $800^\circ\text{C}$  and  $1000^\circ\text{C}$ ) the applicants have found that addition of  $\text{P}_2\text{O}_5$  to compositions allows a broader range of refractory fibres to be produced than had previously been appreciated. They have also found that  $\text{B}_2\text{O}_3$ , previously thought to be

extremely detrimental to refractoriness, has a similar, although lesser, effect and that both  $P_2O_5$  and  $B_2O_3$  may be used in the fibres of WO93/15028.

The applicants have found that the refractoriness of the  $P_2O_5$  and  $B_2O_3$  containing fibres of the present invention is dependent on the sum of the amounts of  $SiO_2$  and  $P_2O_5$  (expressed in wt%)

It appears that a further factor that may be important in determining the refractoriness of a fibre is the percentage of non-bridging oxygens. If this percentage is 61.4% or more (calculated on the basis of the amounts of the components  $SiO_2$ ,  $CaO$ ,  $MgO$ ,  $P_2O_5$ , and  $B_2O_3$ ) the fibres tend to fail shrinkage tests at 800°C and 1000°C (failure being defined as a shrinkage of 3.5% or more).

Accordingly the present invention provides the use of  $P_2O_5$  and/or  $B_2O_3$  as a component to improve the refractoriness of inorganic fibres comprising  $SiO_2$ , and  $CaO$  and/or  $MgO$ , the inorganic fibres having a composition such that

$$SiO_2 + P_2O_5 - (58 + (\text{if } MgO > 10, 0.5 \times (MgO - 10) \text{ else } 0)) > -2.4\text{wt\%}$$

The invention provides further such fibres in which the percentage of non-bridging oxygens is less than 61.4%.

Further features of the invention are apparent from the claims in the light of the following description.

The percentage of non-bridging oxygens (%N.B.O.) is calculated by converting the weight percentages of  $SiO_2$ ,  $CaO$ ,  $MgO$ ,  $P_2O_5$ , and  $B_2O_3$  to molar amounts and inserting these amounts into the equation:-

$$\%N.B.O. = \frac{2 * (CaO + MgO + P_2O_5 + B_2O_3)}{(2 * SiO_2 + CaO + MgO + 5 \times P_2O_5 + 3 \times B_2O_3)} \times 100$$

The reason the amounts of  $CaO$ ,  $MgO$ ,  $P_2O_5$ , and  $B_2O_3$  are doubled in the numerator to this equation is that each contributes two non-bridging oxygens. The reason terms are multiplied in the denominator to this equation is to reflect the number of oxygen atoms each molecular formula possesses.

Table I shows the results of a first set of shrinkage and solubility tests on compositions comprising  $SiO_2$ ,  $CaO$ ,  $MgO$ ,  $P_2O_5$ , and  $B_2O_3$  as main

ingredients. In this table the analysed compositions are normalised to 100%. It is clear from these compositions that where the percentage of non-bridging oxygens calculated on the basis of the amounts of the above named components is greater than 61.4% (those fibres lying above line A of Table I) the fibres fail the shrinkage tests, having shrinkages of greater than 3.5% at either or both of 800°C and 1000°C.

WO93/15028 stressed the importance of alumina content and the fibres lying between lines B and A of Table I show that alumina contents of greater than 1wt% are damaging to the shrinkage properties of fibres.

The applicants have also found that the combined amount of CaO and MgO is important. Those fibres lying between lines C and B have a combined CaO and MgO content of greater than 42wt% and also fail the shrinkage tests.

The fibres below line C have a percentage of non-bridging oxygens less than 61.4%, an alumina content of less than 1wt%, and a combined CaO and MgO content of less than 42wt%. All of these fibres pass the shrinkage tests. These fibres fall within the compositional ranges:-

|                                |                 |
|--------------------------------|-----------------|
| SiO <sub>2</sub>               | 52.4 - 57.85wt% |
| CaO                            | 22.2 - 39.4wt%  |
| MgO                            | 1.96 - 17.4wt%  |
| P <sub>2</sub> O <sub>5</sub>  | 0.82 - 7.8wt%   |
| B <sub>2</sub> O <sub>3</sub>  | 0 - 1.95wt%     |
| Al <sub>2</sub> O <sub>3</sub> | <1wt%           |

The solubility results presented in Table I were obtained by the methods described in WO93/15028 and show a high solubility for all of the fibres produced.

It can be seen that all of the fibres below line C have a K<sub>I</sub> of more than 35 and more than half have a K<sub>I</sub> of more than 40.

Further testing resulted in the data presented in Table II. The data presented are as in table I but an additional column entitled deviation shows the result of looking to the difference between the sum of the SiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> contents and the SiO<sub>2</sub> amount predicted to be needed by WO93/15028 for a fibre to be refractory (shrinkage of less than 3.5% at both 800°C and 1000°C. The figure given is found by calculating the sum

$\text{SiO}_2 + \text{P}_2\text{O}_5 - (58 + (\text{if MgO} > 10, 0.5 \times (\text{MgO} - 10) \text{ else } 0))$

If this is less than -2.4wt% the fibres fail. The fibres that failed are shown in plain text, those that passed in bold text, and those that were difficult to form in italics.

More than 12.5wt%  $\text{P}_2\text{O}_5$  is undesirable as it causes difficulties in making the fibres.

While the above description and the claims refer to  $\text{P}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{MgO}$  it will be clear to the person skilled in the art that the pure materials need not be used and that provision of these components in combined form (e.g. provision of  $\text{P}_2\text{O}_5$  in the form of mixed oxide phosphates) is part of the invention.

Table I

| Code  | Chemical Composition (XRF - Weight percent) |       |      |       |       |      |       |       |       |       |       |       |        |      |     | KI   |      | Shrinkage |     | Solubility (ppm) |       |  |  | Total | CaO+MgO | % N.B.O. |
|-------|---|-------|------|-------|-------|------|-------|-------|-------|-------|-------|-------|--------|------|-----|------|------|-----------|-----|------------------|-------|--|--|-------|---------|----------|
|       | CaO   | MgO   | P2O5 | SiO2  | Al2O3 | Na2O | K2O   | B2O3  | Fe2O3 | ZnO   | SrO   | 800°C | 1000°C | CaO  | MgO | SiO2 | B2O3 |           |     |                  |       |  |  |       |         |          |
|       |   |       |      |       |       |      |       |       |       |       |       |       |        |      |     |      |      |           |     |                  |       |  |  |       |         |          |
| LTP   | 24.95                                       | 19.18 | 3.41 | 51.69 | 0.25  | 0.30 | 0.05  |       | 0.17  | <0.05 | <0.05 | 44.0  | 40.0   | 40.0 | 53  | 98   | 177  |           | 328 | 44.14            | 68.5% |  |  |       |         |          |
| LTP8  | 24.81                                       | 18.66 | 5.10 | 50.42 | 0.38  | 0.31 | <0.05 |       | 0.17  | 0.15  | <0.05 | 43.0  | 23.9   | 38.8 | 59  | 115  | 193  |           | 367 | 43.47            | 68.1% |  |  |       |         |          |
| LTP9  | 25.13                                       | 19.07 | 2.51 | 52.54 | 0.28  | 0.25 | 0.05  |       | 0.17  | <0.05 | <0.05 | 43.9  | 46.8   | 39.1 | 55  | 94   | 174  |           | 323 | 44.20            | 68.0% |  |  |       |         |          |
| LTP11 | 31.83                                       | 12.27 | 3.39 | 51.59 | 0.26  | 0.42 | 0.06  |       | 0.17  | <0.05 | <0.05 | 44.1  | 49.1   |      | 79  | 76   | 200  |           | 355 | 44.11            | 66.1% |  |  |       |         |          |
| LTP16 | 24.48                                       | 17.89 | 2.48 | 54.46 | 0.21  | 0.28 | 0.05  |       | 0.16  | <0.05 | <0.05 | 42.3  | 3.62   | 19.1 | 58  | 90   | 169  |           | 317 | 42.37            | 64.7% |  |  |       |         |          |
| LTP10 | 24.04                                       | 17.78 | 3.31 | 53.85 | 0.31  | 0.26 | 0.05  |       | 0.15  | 0.25  | <0.05 | 41.5  | 3.71   | 4.77 | 56  | 95   | 180  |           | 331 | 41.83            | 64.3% |  |  |       |         |          |
| LTP5  | 24.22                                       | 17.17 | 4.91 | 52.72 | 0.33  | 0.30 | <0.05 |       | 0.14  | 0.21  | <0.05 | 41.0  | 3.63   | 5.39 | 65  | 106  | 191  |           | 362 | 41.40            | 64.1% |  |  |       |         |          |
| LTP17 | 38.39                                       | 5.54  | 3.41 | 51.22 | 0.40  | 0.42 | 0.07  |       | 0.16  | 0.38  | <0.05 | 43.6  | 45.2   | 43.8 | 83  | 32   | 191  |           | 306 | 43.94            | 63.9% |  |  |       |         |          |
| LTP23 | 38.62                                       | 5.56  | 2.57 | 52.23 | 0.34  | 0.46 | 0.07  |       | 0.15  | <0.05 | <0.05 | 44.0  | 42.90  |      | 82  | 29   | 199  |           | 310 | 44.18            | 63.7% |  |  |       |         |          |
| LTP14 | 30.93                                       | 11.01 | 4.90 | 51.96 | 0.30  | 0.45 | 0.05  |       | 0.15  | 0.25  | <0.05 | 41.8  | 3.24   | 3.92 | 78  | 69   | 191  |           | 338 | 41.95            | 63.0% |  |  |       |         |          |
| LTP13 | 11.28                                       | 27.95 | 3.26 | 57.2  | <0.05 | 0.13 | <0.05 |       | 0.17  | <0.05 | <0.05 | 39.4  | 5.72   | 5.26 | 30  | 117  | 188  |           | 335 | 39.23            | 63.0% |  |  |       |         |          |
| LTP12 | 30.93                                       | 11.35 | 3.36 | 53.52 | 0.32  | 0.31 | 0.06  |       | 0.15  | <0.05 | <0.05 | 42.0  | 2.55   | 30.1 | 82  | 72   | 207  |           | 361 | 42.27            | 62.6% |  |  |       |         |          |
| LTP20 | 31.05                                       | 11.35 | 2.52 | 54.14 | 0.32  | 0.31 | 0.06  |       | 0.16  | 0.10  | <0.05 | 42.1  | 3.38   | 29.7 | 85  | 71   | 200  |           | 356 | 42.40            | 62.6% |  |  |       |         |          |
| LTP15 | 36.89                                       | 5.70  | 5.05 | 51.22 | 0.31  | 0.43 | 0.10  |       | 0.16  | 0.13  | <0.05 | 42.5  | 3.41   | 5.03 | 88  | 35   | 204  |           | 327 | 42.59            | 62.2% |  |  |       |         |          |
| LTP3  | 22.89                                       | 16.69 | 6.70 | 52.58 | 0.25  | 0.29 | <0.05 |       | 0.14  | 0.46  | <0.05 | 39.4  | 23.3   | 29.5 | 43  | 166  | 141  |           | 350 | 39.58            | 61.9% |  |  |       |         |          |
| LTP7  | 10.37                                       | 27.85 | 3.29 | 58.18 | <0.05 | 0.15 | <0.05 |       | 0.16  | <0.05 | <0.05 | 38.4  | 10.9   | 15.5 | 36  | 132  | 152  |           | 320 | 38.23            | 61.4% |  |  |       |         |          |
| LTP52 | 24.9  | 11.5  | 4.89 | 54.8  | 2.06  | 0.28 | 0.05  | <0.05 | 1.38  | <0.05 | <0.05 | 32.6  | 32.1   |      | 72  | 74   | 140  |           | 286 | 36.40            | 56.0% |  |  |       |         |          |
| LTP51 | 28.7  | 11    | 1.62 | 56.6  | 1.38  | 0.29 | 0.07  | <0.05 | 0.26  | <0.05 | <0.05 | 37.3  | 3.07   | 3.61 | 82  | 69   | 159  |           | 310 | 39.70            | 58.4% |  |  |       |         |          |
| LTP29 | 40.29                                       | 2.09  | 1.23 | 55.09 | 0.43  | 0.39 | 0.12  |       | 0.19  | 0.17  | <0.05 | 42.0  | 45.9   |      | 76  | 10   | 206  |           | 292 | 42.38            | 58.8% |  |  |       |         |          |
| LTP21 | 36.62                                       | 5.58  | 2.54 | 54.19 | 0.39  | 0.46 | 0.07  |       | 0.15  | <0.05 | <0.05 | 42.0  |        |      | 58  | 34   | 208  |           | 300 | 42.20            | 60.3% |  |  |       |         |          |
| LTP30 | 39.40                                       | 1.96  | 2.22 | 55.25 | 0.45  | 0.41 | 0.10  |       | 0.21  | <0.05 | <0.05 | 41.0  | 1.74   | 2.04 | 72  | 11   | 209  |           | 292 | 41.36            | 57.5% |  |  |       |         |          |
| LTP41 | 31.36                                       | 9.48  | 0.85 | 55.63 | 0.27  | 0.30 | 0.07  | 1.88  | 0.16  | <0.05 | <0.05 | 42.5  | 1.20   | 2.32 | 87  | 60   | 194  | 20        | 361 | 40.84            | 60.0% |  |  |       |         |          |
| LTP6  | 29.83                                       | 10.45 | 3.34 | 55.65 | 0.21  | 0.32 | 0.05  |       | 0.15  | <0.05 | <0.05 | 40.2  | 1.89   | 2.76 | 65  | 52   | 172  |           | 289 | 40.28            | 59.0% |  |  |       |         |          |
| LTP34 | 30.44                                       | 9.81  | 1.68 | 57.3  | 0.25  | 0.31 | 0.07  |       | 0.15  | <0.05 | <0.05 | 40.1  | 1.40   | 1.79 | 76  | 51   | 188  |           | 315 | 40.25            | 58.0% |  |  |       |         |          |
| LTP43 | 30.51                                       | 9.68  | 1.68 | 56.19 | 0.28  | 0.32 | 0.07  | 1.11  | 0.15  | <0.05 | <0.05 | 41.1  | 0.97   | 1.84 | 62  | 66   | 187  | 12        | 327 | 40.19            | 58.8% |  |  |       |         |          |
| LTP42 | 30.55                                       | 9.56  | 0.86 | 57.13 | 0.27  | 0.33 | 0.07  | 1.08  | 0.15  | <0.05 | <0.05 | 41.1  | 1.04   | 1.81 | 75  | 65   | 192  | 12        | 344 | 40.12            | 58.2% |  |  |       |         |          |
| LTP47 | 22.2  | 17.4  | 3.98 | 55.2  | 0.31  | 0.31 | 0.05  | <0.05 | 0.1   | <0.05 | <0.05 | 39.3  | 1.97   | 2.14 | 58  | 104  | 197  |           | 359 | 39.60            | 61.0% |  |  |       |         |          |
| LTP38 | 34.82                                       | 4.73  | 0.82 | 57.84 | 0.31  | 0.30 | 0.08  | 0.94  | 0.15  | <0.05 | <0.05 | 40.3  | 1.07   | 1.40 | 83  | 25   | 175  | 9         | 292 | 39.56            | 55.4% |  |  |       |         |          |
| LTP2  | 23.35                                       | 16.10 | 4.87 | 54.25 | 0.46  | 0.24 | <0.05 |       | 0.16  | 0.58  | <0.05 | 38.8  | 2.24   | 3.05 | 53  | 96   | 167  |           | 316 | 39.45            | 60.8% |  |  |       |         |          |
| LTP39 | 34.35                                       | 4.73  | 1.67 | 57.39 | 0.27  | 0.30 | 0.08  | 1.06  | 0.14  | <0.05 | <0.05 | 40.0  | 1.47   | 1.93 | 32  | 33   | 203  | 16        | 284 | 39.08            | 55.2% |  |  |       |         |          |
| LTP1  | 23.29                                       | 15.66 | 3.33 | 57.01 | 0.24  | 0.22 | 0.06  |       | 0.14  | <0.05 | 0.05  | 38.7  | 1.31   | 1.77 | 63  | 89   | 175  |           | 327 | 38.94            | 58.7% |  |  |       |         |          |
| LTP48 | 32  | 6.87  | 7.8  | 52.4  | 0.52  | 0.34 | 0.05  | <0.05 | 0.15  | 0.18  | <0.05 | 38.2  | 1.24   | 1.53 | 84  | 48   | 205  |           | 337 | 38.87            | 57.7% |  |  |       |         |          |
| LTP40 | 33.67                                       | 4.75  | 0.86 | 57.85 | 0.38  | 0.31 | 0.08  | 1.95  | 0.15  | <0.05 | <0.05 | 40.0  | 1.15   | 2.39 | 40  | 32   | 194  | 25        | 291 | 38.42            | 54.5% |  |  |       |         |          |
| LTP26 | 33.69                                       | 4.56  | 3.75 | 56.95 | 0.36  | 0.43 | 0.06  |       | 0.14  | 0.07  | <0.05 | 38.0  | 1.22   | 1.40 | 91  | 28   | 193  |           | 312 | 38.25            | 54.0% |  |  |       |         |          |
| LTP27 | 28.91                                       | 9.33  | 3.66 | 57.32 | 0.22  | 0.36 | 0.05  |       | 0.14  | <0.05 | <0.05 | 38.2  | 0.99   | 1.16 | 67  | 48   | 173  |           | 288 | 38.24            | 55.5% |  |  |       |         |          |
| LTP46 | 28.4  | 8.69  | 2.67 | 59    | 0.29  | 0.33 | 0.06  | <0.05 | 0.13  | <0.05 | <0.05 | 36.9  | 0.91   | 0.99 | 71  | 46   | 175  |           | 292 | 37.09            | 53.3% |  |  |       |         |          |

TABLE II (Part I)

| Code  | Chemical Composition (XRF - Weight percent) |       |       |       |       |      |      |      |       |      |     |       | KI    | Shrinkage |           | Solubility (ppm) |     |      |      | CaO+MgO | % N.B.O. |       |
|---|---|-------|-------|-------|-------|------|------|------|-------|------|-----|-------|-------|-----------|-----------|------------------|-----|------|------|---------|----------|-------|
|   | CaO   | MgO   | P2O5  | SiO2  | Al2O3 | Na2O | K2O  | B2O3 | Fe2O3 | ZrO2 | SiO | 800°C |       | 1000°C    | Deviation | CaO              | MgO | SiO2 | B2O3 |         |          | Total |
|   |   |       |       |       |       |      |      |      |       |      |     |       |       |           |           |                  |     |      |      |         |          |       |
| LTP   |   |       |       |       |       |      |      |      |       |      |     |       |       |           |           |                  |     |      |      |         |          |       |
| LTP 8   | 24.95                                       | 19.18 | 3.41  | 51.69 | 0.25  | 0.30 | 0.05 |      | 0.17  |      |     | 43.99 | 40.00 | -7.49     | 53        | 98               | 177 |      | 328  | 44.14   | 68.5%    |       |
| LTP11   | 25.13                                       | 19.07 | 2.51  | 52.54 | 0.28  | 0.25 | 0.05 |      | 0.17  |      |     | 43.94 | 46.80 | -7.48     | 55        | 94               | 174 |      | 323  | 44.20   | 68.0%    |       |
| LTP49   | 32.35                                       | 6.74  |       | 50.54 | 0.57  | 0.40 | 0.08 | 9.17 | 0.14  |      |     | 47.60 | 2.65  | -7.46     | 79        | 41               | 214 | 129  | 463  | 39.09   | 62.1%    |       |
| LTP 9   | 24.81                                       | 18.66 | 5.10  | 50.42 | 0.38  | 0.31 |      |      | 0.17  | 0.15 |     | 43.03 | 23.90 | -6.81     | 59        | 115              | 193 |      | 367  | 43.47   | 68.1%    |       |
| LTP67   | 15.17                                       | 25.18 | 5.06  | 54.00 | 0.19  | 0.25 |      |      | 0.15  |      |     | 40.22 | 5.70  | -6.53     |           |                  |     |      |      | 40.35   | 64.9%    |       |
| LTP13   | 11.28                                       | 27.95 | 3.26  | 57.20 |       | 0.13 |      |      | 0.17  |      |     | 39.36 | 5.72  | -6.51     | 30        | 117              | 188 |      | 335  | 39.23   | 63.0%    |       |
| LTP62   | 14.99                                       | 24.54 | 2.52  | 57.24 | 0.35  | 0.19 |      |      | 0.16  |      |     | 39.02 | 4.48  | -5.51     | 25        | 66               | 119 |      | 210  | 39.53   | 62.3%    |       |
| LTP 7   | 10.37                                       | 27.85 | 3.29  | 58.18 |       | 0.15 |      |      | 0.16  |      |     | 38.37 | 10.90 | -5.46     | 36        | 132              | 152 |      | 320  | 38.23   | 61.4%    |       |
| LTP10   | 24.48                                       | 17.89 | 2.48  | 54.46 | 0.21  | 0.28 | 0.05 |      | 0.16  |      |     | 42.28 | 3.62  | -5.01     | 58        | 90               | 169 |      | 317  | 42.37   | 64.7%    |       |
| LTP 4   | 24.04                                       | 17.78 | 3.31  | 53.85 | 0.31  | 0.26 | 0.05 |      | 0.15  | 0.25 |     | 41.52 | 3.71  | -4.73     | 56        | 95               | 180 |      | 331  | 41.83   | 64.3%    |       |
| LTP16   | 31.83                                       | 12.27 | 3.39  | 51.59 | 0.26  | 0.42 | 0.06 |      | 0.17  |      |     | 44.07 | 49.10 | -4.15     | 79        | 76               | 200 |      | 355  | 44.11   | 66.1%    |       |
| LTP 5   | 24.22                                       | 17.17 | 4.91  | 52.72 | 0.33  | 0.30 |      |      | 0.14  | 0.21 |     | 41.04 | 3.63  | -3.96     | 65        | 106              | 191 |      | 362  | 41.40   | 64.1%    |       |
| LTP59   | 32.13                                       | 10.47 | 12.93 | 41.37 | 2.31  | 0.56 | 0.05 |      | 0.17  |      |     | 38.59 | 43.20 | -3.94     | 42        | 41               | 179 |      | 262  | 42.60   | 69.3%    |       |
| LTP50   | 31.00                                       | 10.40 |       | 54.50 | 0.36  | 0.31 | 0.08 | 3.19 | 0.16  |      |     | 44.26 | 29.80 | -3.70     | 79        | 58               | 200 | 30   | 367  | 41.40   | 62.0%    |       |
| LTP17   | 36.39                                       | 5.54  | 3.41  | 51.22 | 0.40  | 0.42 | 0.07 |      | 0.16  | 0.38 |     | 43.62 | 45.20 | -3.37     | 83        | 32               | 191 |      | 306  | 43.94   | 63.9%    |       |
| LTP56   | 34.38                                       | 9.46  | 14.72 | 40.02 | 0.72  | 0.55 |      |      | 0.16  |      |     | 42.95 | 9.98  | -3.26     | 60        | 57               | 196 |      | 313  | 43.84   | 70.5%    |       |
| LTP23   | 38.62                                       | 5.56  | 2.57  | 52.23 | 0.34  | 0.46 | 0.07 |      | 0.15  |      |     | 44.03 | 42.90 | -3.20     | 82        | 29               | 199 |      | 310  | 44.18   | 63.7%    |       |
| LTP57   | 34.73                                       | 9.55  | 19.83 | 35.24 | 0.23  | 0.26 |      |      | 0.15  |      |     | 44.08 | -     | -2.93     |           |                  |     |      | 0    | 44.28   | 71.0%    |       |
| LTP70   | 24.38                                       | 14.20 |       | 57.52 | 0.44  | 0.18 | 0.08 | 3.01 | 0.18  |      |     | 40.97 | 3.63  | -2.58     | 75        | 73               | 255 | 21   | 424  | 38.58   | 58.7%    |       |
| LTP63   | 14.61                                       | 22.87 | 2.53  | 59.45 | 0.27  | 0.12 |      |      | 0.16  |      |     | 37.06 | 9.57  | -2.46     | 17        | 108              | 83  |      | 208  | 37.48   | 58.4%    |       |
| Above here compositions have deviation of more than 2.4wt%  |   |       |       |       |       |      |      |      |       |      |     |       |       |           |           |                  |     |      |      |         |          |       |
| LTP54   | 29.40                                       | 8.73  | 14.55 | 46.68 | 0.07  | 0.44 |      |      | 0.13  |      |     | 38.43 | -     | 3.23      |           |                  |     |      |      | 38.13   | 60.1%    |       |
| LTP61   | 32.46                                       | 9.86  | 14.02 | 42.67 | 0.09  | 0.70 | 0.05 |      | 0.15  |      |     | 42.89 | 3.44  | -1.31     |           |                  |     |      |      | 42.32   | 67.4%    |       |
| LTP60   | 31.46                                       | 9.58  | 12.64 | 44.91 | 0.69  | 0.54 | 0.05 |      | 0.14  |      |     | 40.25 | -     | -0.45     |           |                  |     |      |      | 41.04   | 64.8%    |       |
| Above here compositions have P2O5 content more than 12.5wt% |   |       |       |       |       |      |      |      |       |      |     |       |       |           |           |                  |     |      |      |         |          |       |
| LTP52   | 24.93                                       | 11.52 | 4.90  | 54.88 | 2.06  | 0.28 | 0.05 |      | 1.38  |      |     | 32.66 | 32.10 | 1.02      | 72        | 74               | 140 |      | 286  | 36.45   | 56.1%    |       |
| LTP51   | 28.72                                       | 11.01 | 1.62  | 56.65 | 1.38  | 0.29 | 0.07 |      | 0.26  |      |     | 37.33 | 3.07  | -0.24     | 82        | 69               | 159 |      | 310  | 39.73   | 58.4%    |       |
| Above here fibres have Al2O3 content above 1 wt%            |   |       |       |       |       |      |      |      |       |      |     |       |       |           |           |                  |     |      |      |         |          |       |
| LTP15   | 36.89                                       | 5.70  | 5.05  | 51.22 | 0.31  | 0.43 | 0.10 |      | 0.16  | 0.13 |     | 42.50 | 3.41  | -1.72     | 88        | 35               | 204 |      | 327  | 42.59   | 62.2%    |       |
| LTP14   | 30.93                                       | 11.01 | 4.90  | 51.96 | 0.30  | 0.45 | 0.05 |      | 0.15  | 0.25 |     | 41.85 | 3.24  | -1.65     | 78        | 69               | 191 |      | 338  | 41.95   | 63.0%    |       |
| LTP58   | 32.93                                       | 9.77  | 12.01 | 44.34 | 0.19  | 0.53 | 0.05 |      | 0.19  |      |     | 42.90 | 2.62  | -1.65     | 57        | 42               | 223 |      | 322  | 42.70   | 67.0%    |       |
| LTP55   | 32.58                                       | 9.47  | 9.65  | 46.79 | 0.84  | 0.46 | 0.05 |      | 0.17  |      |     | 40.88 | 1.72  | -1.56     | 71        | 54               | 203 |      | 338  | 42.05   | 65.1%    |       |
| LTP53   | 29.34                                       | 9.84  | 9.58  | 50.26 | 0.17  | 0.56 | 0.05 |      | 0.15  | 0.05 |     | 39.45 | 0.01  | 1.84      | 71        | 83               | 222 |      | 376  | 39.18   | 60.1%    |       |
| Above here SiO2 content less than 52wt%                     |   |       |       |       |       |      |      |      |       |      |     |       |       |           |           |                  |     |      |      |         |          |       |



TABLE II (Part 2)

| Code   | Chemical Composition (XRF - Weight percent) |       |      |       |       |      |      |      |       |      |      | KI    | Shrinkage |        | Solubility (ppm) |     |      |      | CaO+MgO | % N.B.O. |
|--|---|-------|------|-------|-------|------|------|------|-------|------|------|-------|-----------|--------|------------------|-----|------|------|---------|----------|
|  | CaO   | MgO   | P2O5 | SiO2  | Al2O3 | Na2O | K2O  | B2O3 | Fe2O3 | ZnO  | SiO  |       | 800°C     | 1000°C | CaO              | MgO | SiO2 | B2O3 | Total   |          |
| I.TP   | 22.89                                       | 16.89 | 6.70 | 52.58 | 0.25  | 0.29 |      |      | 0.14  | 0.46 |      | 39.37 | 23.30     | 28.50  | 43               | 166 | 141  |      | 350     | 61.9%    |
| I.TP3  | 31.05                                       | 11.35 | 2.52 | 54.14 | 0.32  | 0.31 | 0.06 |      | 0.16  | 0.10 |      | 42.13 | 3.38      | 29.70  | 85               | 71  | 200  |      | 356     | 61.6%    |
| I.TP2  | 23.35                                       | 16.10 | 4.87 | 54.25 | 0.46  | 0.24 |      |      | 0.16  | 0.58 |      | 38.77 | 2.24      | 3.05   | 53               | 96  | 167  |      | 316     | 60.8%    |
| I.TP12   | 30.93                                       | 11.35 | 3.36 | 53.52 | 0.32  | 0.31 | 0.06 |      | 0.15  |      |      | 42.00 | 2.55      | 30.10  | 82               | 72  | 207  |      | 361     | 62.6%    |
| I.TP21   | 36.62                                       | 5.58  | 2.54 | 54.19 | 0.39  | 0.46 | 0.07 |      | 0.15  |      |      | 41.95 | -         | 35.50  | 58               | 34  | 208  |      | 300     | 60.3%    |
| I.TP48   | 31.90                                       | 6.85  | 7.78 | 52.24 | 0.52  | 0.34 | 0.05 |      | 0.15  | 0.18 |      | 38.10 | 1.24      | 1.53   | 84               | 48  | 205  |      | 337     | 57.7%    |
| Above here SiO2 content 52wt% to less than 55wt% |   |       |      |       |       |      |      |      |       |      |      |       |           |        |                  |     |      |      |         |          |
| I.TP47   | 22.30                                       | 17.48 | 4.00 | 55.45 | 0.31  | 0.31 | 0.05 |      | 0.10  |      |      | 39.52 | 1.97      | 2.14   | 58               | 104 | 197  |      | 359     | 61.0%    |
| I.TP64   | 20.81                                       | 18.41 | 2.52 | 57.63 | 0.22  | 0.26 |      |      | 0.14  |      |      | 39.04 | 3.01      | 3.73   | 46               | 76  | 197  |      | 319     | 59.7%    |
| I.TP68   | 20.08                                       | 18.77 | 4.55 | 55.92 | 0.30  | 0.24 |      |      | 0.14  |      |      | 38.49 | 3.90      | 4.16   | 51               | 89  | 226  |      | 366     | 60.2%    |
| I.TP29   | 40.29                                       | 2.09  | 1.23 | 55.09 | 0.43  | 0.39 | 0.12 |      | 0.19  | 0.17 |      | 42.03 | 45.85     | -      | 76               | 10  | 206  |      | 292     | 58.8%    |
| I.TP41   | 31.36                                       | 9.48  | 0.85 | 55.63 | 0.27  | 0.30 | 0.07 | 1.88 | 0.16  |      |      | 42.55 | 1.20      | 2.32   | 87               | 60  | 194  | 20   | 361     | 60.0%    |
| I.TP71   | 38.31                                       | 0.65  |      | 56.51 | 0.55  | 0.20 | 0.09 | 3.54 | 0.14  |      |      | 41.69 | 0.59      | 1.43   | 73               | 2   | 278  | 55   | 408     | 54.9%    |
| I.TP30   | 39.40                                       | 1.96  | 2.22 | 55.25 | 0.45  | 0.41 | 0.10 |      | 0.21  |      |      | 40.96 | 1.74      | 2.04   | 72               | 11  | 209  |      | 292     | 57.5%    |
| I.TP1  | 23.29                                       | 15.66 | 3.33 | 57.01 | 0.24  | 0.22 | 0.06 |      | 0.14  |      |      | 40.96 | 1.74      | 2.04   | 63               | 89  | 175  |      | 327     | 58.7%    |
| I.TP43   | 30.51                                       | 9.68  | 1.68 | 56.19 | 0.28  | 0.32 | 0.07 | 1.11 | 0.15  |      | 0.05 | 41.13 | 0.97      | 1.84   | 62               | 66  | 187  | 12   | 327     | 58.8%    |
| I.TP37   | 35.40                                       | 4.77  |      | 57.92 | 0.31  | 0.31 | 0.09 | 1.05 | 0.15  |      |      | 40.99 | 1.57      | 2.13   | 37               | 30  | 195  | 13   | 275     | 56.1%    |
| I.TP32   | 30.01                                       | 8.53  |      | 57.95 | 0.32  | 0.23 | 0.09 | 2.69 | 0.18  |      |      | 40.92 | 1.68      | 2.83   | 80               | 46  | 184  | 24   | 334     | 56.3%    |
| I.TP73   | 36.93                                       | 0.62  |      | 57.96 | 0.49  | 0.23 | 0.09 | 3.54 | 0.13  |      |      | 40.43 | 1.23      | 3.00   | 76               | 2   | 264  | 40   | 382     | 52.6%    |
| I.TP42   | 30.55                                       | 9.56  | 0.86 | 57.13 | 0.27  | 0.33 | 0.07 | 1.08 | 0.15  |      |      | 41.06 | 1.04      | 1.81   | 75               | 65  | 192  | 12   | 344     | 58.2%    |
| I.TP38   | 34.82                                       | 4.73  | 0.82 | 57.84 | 0.31  | 0.30 | 0.08 | 0.94 | 0.15  |      |      | 40.26 | 1.07      | 1.40   | 83               | 25  | 175  | 9    | 292     | 55.4%    |
| I.TP40   | 33.67                                       | 4.75  | 0.86 | 57.85 | 0.38  | 0.31 | 0.08 | 1.95 | 0.15  |      |      | 40.00 | 1.15      | 2.39   | 40               | 32  | 194  | 25   | 291     | 54.5%    |
| I.TP6  | 29.83                                       | 10.45 | 3.34 | 55.65 | 0.21  | 0.32 | 0.05 |      | 0.15  |      |      | 40.23 | 1.89      | 2.76   | 65               | 52  | 172  |      | 289     | 59.0%    |
| I.TP69   | 19.17                                       | 17.56 | 4.66 | 57.93 | 0.31  | 0.23 |      |      | 0.13  |      |      | 36.34 | 1.23      | 1.68   | 49               | 88  | 241  |      | 378     | 56.5%    |
| I.TP34   | 30.44                                       | 9.81  | 1.68 | 57.30 | 0.25  | 0.31 | 0.07 |      | 0.15  |      |      | 40.13 | 1.40      | 1.79   | 76               | 51  | 188  |      | 315     | 58.0%    |
| I.TP39   | 34.35                                       | 4.73  | 1.67 | 57.39 | 0.27  | 0.30 | 0.08 | 1.06 | 0.14  |      |      | 39.98 | 1.47      | 1.93   | 32               | 33  | 203  | 16   | 284     | 55.2%    |
| I.TP26   | 33.69                                       | 4.56  | 3.73 | 56.95 | 0.36  | 0.43 | 0.06 |      | 0.14  | 0.07 |      | 38.02 | 1.22      | 1.40   | 91               | 28  | 193  |      | 312     | 54.0%    |
| I.TP27   | 28.91                                       | 9.33  | 3.66 | 57.32 | 0.22  | 0.36 | 0.05 |      | 0.14  |      |      | 38.21 | 0.99      | 1.16   | 67               | 48  | 173  |      | 288     | 55.5%    |
| Above here SiO2 content 55wt% to less than 58wt% |   |       |      |       |       |      |      |      |       |      |      |       |           |        |                  |     |      |      |         |          |

TABLE II (Part 3)

| Code  | Chemical Composition (XRF - Weight percent) |       |      |       |       |      |      |      |       |      |      | KI    | Shrinkage |        | Solubility (ppm) |     |     |      | Total | CaO+MgO | % N.B.O. |       |
|-------|---|-------|------|-------|-------|------|------|------|-------|------|------|-------|-----------|--------|------------------|-----|-----|------|-------|---------|----------|-------|
|       | CaO   | MgO   | P2O5 | SiO2  | Al2O3 | Na2O | K2O  | B2O3 | Fe2O3 | ZrO2 | SiO  |       | 800°C     | 1000°C | Deviation        | CaO | MgO | SiO2 |       |         |          | B2O3  |
| LTP66 | 15.65                                       | 21.16 | 4.38 | 58.17 | 0.24  | 0.25 |      |      | 0.15  |      |      | 36.58 | 2.65      | 3.19   | -1.03            | 30  | 84  | 169  |       | 283     | 36.81    | 57.7% |
| LTP65 | 20.36                                       | 17.74 | 2.50 | 58.75 | 0.30  | 0.22 |      |      | 0.13  |      |      | 37.72 | 2.28      | 2.37   | -0.62            | 41  | 68  | 185  |       | 294     | 38.10    | 57.6% |
| LTP72 | 22.67                                       | 13.60 |      | 59.64 | 0.37  | 0.27 | 0.06 | 3.25 | 0.14  |      |      | 39.11 | 3.37      | 6.16   | -0.16            | 49  | 56  | 197  | 23    | 325     | 36.27    | 55.0% |
| LTP35 | 32.72                                       | 4.76  |      | 58.60 | 0.28  | 0.31 | 0.08 | 3.09 | 0.15  |      |      | 40.40 | 1.65      | 3.85   | 0.60             | 88  | 26  | 179  | 29    | 322     | 37.48    | 53.5% |
| LTP31 | 28.30                                       | 9.20  |      | 58.70 | 0.28  | 0.29 | 0.06 | 3.00 | 0.18  |      |      | 40.29 | 3.15      | 4.88   | 0.70             | 91  | 60  | 205  | 31    | 387     | 37.50    | 55.1% |
| LTP36 | 33.37                                       | 4.82  |      | 58.90 | 0.27  | 0.30 | 0.08 | 2.10 | 0.15  |      |      | 40.13 | 1.50      | 3.12   | 0.90             | 37  | 33  | 198  | 25    | 293     | 38.19    | 53.9% |
| LTP33 | 30.20                                       | 9.03  |      | 59.01 | 0.27  | 0.28 | 0.08 | 0.96 | 0.17  |      |      | 40.02 | 2.16      | 2.74   | 1.01             | 88  | 52  | 193  | 10    | 343     | 39.23    | 56.1% |
| LTP44 | 29.05                                       | 6.88  |      | 59.81 | 0.35  | 0.36 | 0.07 | 3.16 | 0.13  |      | 0.19 | 38.82 | 1.60      | 2.71   | 1.81             | 89  | 44  | 193  | 32    | 358     | 35.93    | 52.1% |
| LTP45 | 24.10                                       | 11.40 |      | 62.48 | 0.54  | 0.24 | 0.06 | 1.04 | 0.15  |      |      | 35.76 | 2.17      | 3.15   | 3.78             | 81  | 65  | 189  | 10    | 345     | 35.50    | 51.3% |
| LTP46 | 28.52                                       | 8.73  | 2.68 | 59.25 | 0.29  | 0.33 | 0.06 |      | 0.13  |      |      | 37.06 | 0.91      | 0.99   | 3.93             | 71  | 46  | 175  |       | 292     | 37.25    | 53.3% |

Above here SiO2 content: 58wt% or more

Above here SiO2 content 58wt% or more

CLAIMS

1. The use of  $P_2O_5$  or  $B_2O_3$  as a component to improve the refractoriness of inorganic fibres comprising  $SiO_2$ , and CaO and/or MgO, to produce inorganic fibres having a composition having a shrinkage of less than 3.5% when exposed to  $1000^\circ C$  for 24 hours and having a shrinkage of less than 3.5% when exposed to  $800^\circ C$  for 24 hours, the fibres having a composition such that

$$SiO_2 + P_2O_5 - (58 + (\text{if } MgO > 10, 0.5 \times (MgO - 10) \text{ else } 0)) > -2.4wt\%$$

2. The use of  $P_2O_5$  or  $B_2O_3$  as a component to improve the refractoriness of inorganic fibres as claimed in claim 1 in which the percentage of non-bridging oxygens is less than 61.4%.
3. The use of  $P_2O_5$  or  $B_2O_3$  as a component to improve the refractoriness of inorganic fibres as claimed in claim 1 or claim 2 in which the fibres fall within the compositional range:-

|          |             |
|----------|-------------|
| $SiO_2$  | 44 or more  |
| CaO      | 20 - 40wt%  |
| MgO      | 0 - 18wt%   |
| $P_2O_5$ | 0 - 12.5wt% |
| $B_2O_3$ | 0 - 4wt%    |

4. The use of  $P_2O_5$  or  $B_2O_3$  as a component to improve the refractoriness of inorganic fibres as claimed in claim 3 in which the fibres fall within the compositional range:-

|           |  |
|-----------|--|
| $SiO_2$   | 52 - <58wt% [52 - <58+0.5*(MgO-10)wt% if<br>MgO > 10wt%] |
| CaO       | 22 - 40wt%   |
| MgO       | 0 - 17.5wt%  |
| MgO + CaO | < 42wt%  |
| $P_2O_5$  | 0.5 - 10wt%  |
| $B_2O_3$  | 0 - 2wt%   |

5. The use of  $P_2O_5$  or  $B_2O_3$  as a component to improve the refractoriness of inorganic fibres as claimed in claim 3 in which the fibres fall within the compositional range:-

|         |               |
|---------|---------------|
| $SiO_2$ | 44.34 - 62.48 |
|---------|---------------|

|                               |                 |
|-------------------------------|-----------------|
| CaO                           | 20.36 - 39.4wt% |
| MgO                           | 0.62 - 21.16wt% |
| P <sub>2</sub> O <sub>5</sub> | 0 - 12.01wt%    |
| B <sub>2</sub> O <sub>3</sub> | 0 - 3.54wt%     |

6. Saline soluble inorganic fibres having a shrinkage of less than 3.5% when exposed to 1000°C for 24 hours and having a shrinkage of less than 3.5% when exposed to 800°C for 24 hours, in which:-

$$\text{SiO}_2 + \text{P}_2\text{O}_5 - (58 + (\text{if MgO} > 10, 0.5 \times (\text{MgO} - 10) \text{ else } 0)) > -2.4\text{wt}\%$$

7. Saline soluble inorganic fibres as claimed in claim 6 comprising:-

|                               |             |
|-------------------------------|-------------|
| SiO <sub>2</sub>              | 44 or more  |
| CaO                           | 20 - 40wt%  |
| MgO                           | 0 - 18wt%   |
| P <sub>2</sub> O <sub>5</sub> | 0 - 12.5wt% |
| B <sub>2</sub> O <sub>3</sub> | 0 - 4wt%    |

8. Saline soluble inorganic fibres as claimed in claim 7 comprising:-

|                               |  |
|-------------------------------|--|
| SiO <sub>2</sub>              | 52 - <58wt% [52 - <58+0.5'(MgO-10)wt% if<br>MgO > 10wt%] |
| CaO                           | 22 - 40wt%   |
| MgO                           | 0 - 17.5wt%  |
| MgO + CaO                     | < 42wt%  |
| P <sub>2</sub> O <sub>5</sub> | 0.5 - 10wt%  |
| B <sub>2</sub> O <sub>3</sub> | 0 - 2wt%   |

and in which the percentage of non-bridging oxygens calculated on the basis of the amounts of the above named components is less than 61.4%.

9. Saline soluble inorganic fibres as claimed in claim 7 comprising:-

|                               |                 |
|-------------------------------|-----------------|
| SiO <sub>2</sub>              | 44.34 - 62.48   |
| CaO                           | 20.36 - 39.4wt% |
| MgO                           | 0.62 - 21.16wt% |
| P <sub>2</sub> O <sub>5</sub> | 0 - 12.01wt%    |
| B <sub>2</sub> O <sub>3</sub> | 0 - 3.54wt%     |

10. Saline soluble inorganic fibres as claimed in claim 6 in which the fibres have a composition:-

|                                |                 |
|--------------------------------|-----------------|
| SiO <sub>2</sub>               | 52.4 - 57.85wt% |
| CaO                            | 22.2 - 39.4wt%  |
| MgO                            | 1.96 - 17.4wt%  |
| P <sub>2</sub> O <sub>5</sub>  | 0.82 - 7.8wt%   |
| B <sub>2</sub> O <sub>3</sub>  | 0 - 1.95wt%     |
| Al <sub>2</sub> O <sub>3</sub> | <1wt%           |

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# INTERNATIONAL SEARCH REPORT

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| Internat. Application No<br><b>PCT/GB 97/01667</b> |
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**A. CLASSIFICATION OF SUBJECT MATTER**  
**IPC 6 C03C13/00**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
**IPC 6 C03C**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "&" document member of the same patent family

Date of the actual completion of the international search

**22 September 1997**

Date of mailing of the international search report

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PCT/GB 97/01667

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